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LOW TEMPERATURE OXIDATION CHEMISTRY OF JP-8

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In an effort to develop surrogate fuels for engine modeling and development, this project is examining the low and intermediate temperature oxidation chemistry of JP-8, potential JP-8 surrogates, and their components at elevated pressure. Experiments are being run in a pressurized flow reactor (PFR) and/or a single cylinder research engine. A fundamental understanding of the preignition chemistry of high molecular weight hydrocarbons, similar to, if not including, components of real fuels, is necessary to advance the development of fuel surrogates. This project is providing information necessary to determine the chemical reaction mechanisms of such hydrocarbons. In prior work, we developed a four-component JP-8 surrogate and a four-component gasoline surrogate, and we characterized their reactivity in the low and intermediate temperature regimes (600 – 800 K) using our PFR facility to oxidize the fuels and our gas chromatography/mass spectrometer facility to measure the intermediate species. This year, we examined the behavior of jet fuels and the JP-8 surrogate in our single cylinder engine facility, and we used our PFR to explore the autoignition of Fischer-Tropsch JP-8 and a potential Fischer-Tropsch JP-8 surrogate.

For the engine experiments, the test facility consists of a 611 cm³, single cylinder, Waukesha Motor Corporation Model 48D, Cooperative Fuels Research engine directly coupled to a GE CD258AT DC motor dynamometer. The engine has an 8.255 cm cylinder bore and an 11 cm piston stroke. The compression ratio was fixed at 16:1, the inlet manifold pressure was set at 1.0 bar, and the engine was operated at a speed of 800 rpm. Experiments were run at an inlet temperature of 476 K, which is above the boiling point of the fuels tested, thereby eliminating concerns about fuel condensation. Each test fuel was injected into the air stream of the heated inlet manifold well upstream of the intake valve to assure complete vaporization and mixing. The autoignition behavior of these fuels was monitored by measuring the in-cylinder pressure with a water cooled, piezoelectric pressure transducer coupled to a charge amplifier.

Three JP-8 samples and three Jet A samples, acquired from Wright-Patterson Air Force Base and described in Table 1, were stressed to the point of autoignition in the engine at equivalence ratios of 0.28, 0.35, 0.42, and 0.49. The low and intermediate temperature reactivity of the samples had been measured in the PFR facility, and these engine experiments were run to provide additional information relevant for modeling. Figs. 1 and 2 show the pressure traces of the JP-8 and Jet A samples, respectively, as functions of the crank angle degree (CAD).

Table 1: Engine text matrix of jet fuel samples

Fuel	% Alkanes	% Aromatics	% Alkenes	Cetane Index
*JP-8 #3684	80.6	18.1	1.3	44.8
JP-8 #3804	79.8	9.7	0.5	47.0
JP-8 #3773	83.4	15.9	0.7	46.0
*Jet A #3593	79.1	19.0	1.9	44.4
Jet A #3602	75.1	24.0	0.9	40.7
Jet A #3638	86.6	12.0	1.4	45.9

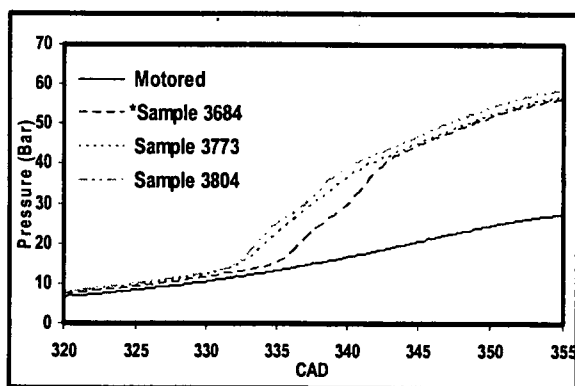*Specific samples that matched the "average" composition and properties of JP-8 and Jet A

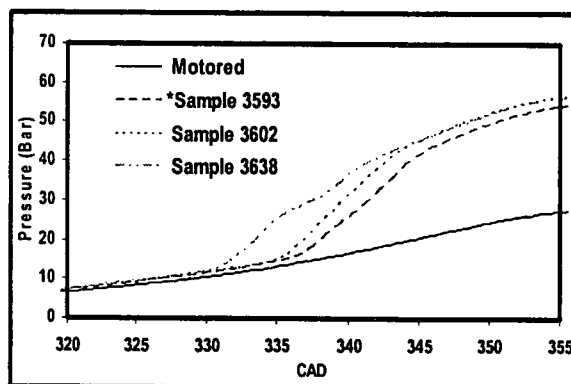Figure 1: Autoignition of JP-8 samples at φ = 0.49, CR = 16, and T_{in} = 476 K

Figure 2: Autoignition of Jet A samples at φ =0.49, CR = 16, and T_{in} = 476 K

The differences in autoignition behavior are due to differences in the preignition chemistry, as defined by fuel properties, such as aromatic content, cycloalkane content, and cetane index (CI). The results showed that increasing aromatic content delayed ignition timing. For the JP-8 samples, increasing cetane index shortened ignition timing. However, the Jet A samples, 3593 and 3602, with significantly different CI values (44.4 and 40.7) had essentially the same ignition time, although they had similar aromatic content. This confirms our prior conclusion that the ASTM formula (D 976) used for calculating these CI indices may not be valid for all jet fuels. Furthermore, comparison of results from the four equivalence ratios showed that increasing equivalence ratio to closer to 1 advanced the ignition timing, as expected.

n-Dodecane, iso-cetane, methylcyclohexane, and 1-methylnaphthalene (the JP-8 surrogate components) were run in the engine as representative components for linear alkanes, branched alkanes, cycloalkanes, and aromatics, respectively. Methylcyclohexane and 1-methylnaphthalene showed no reactivity as neat fuels so they were run with n-dodecane as a reaction initiator. For comparison a mixture of n-dodecane and iso-cetane was also run. Figs. 3 and 4 show the measured pressure traces. Mixes 1, 2, and 3 had CI values of 41.0, 42.2, and 40.8, respectively. Fig. 4 shows that the difference in ignition time for Mixes 1 and 2, with a CI difference of 1.2, is very small. However, Mix 3, with almost the same CI as Mix 1, showed a significantly different ignition time. This demonstrates that the autoignition behavior of mixtures cannot simply be predicted by CI values.
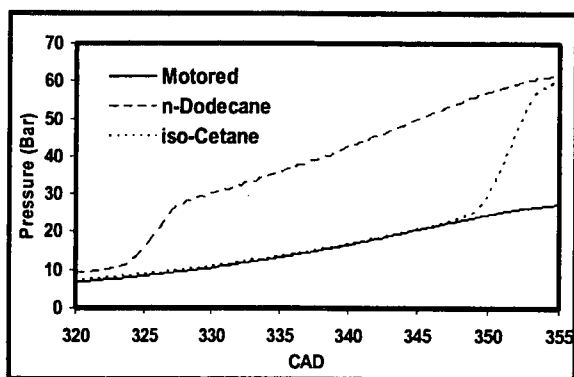

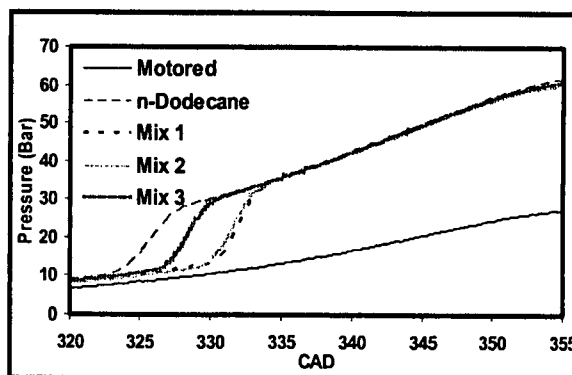Figure 3: Autoignition of neat n-dodecane and neat iso-cetane at φ = 0.49, CR = 16, and T_{in} = 476 K

Figure 4: Autoignition of binary mixtures at φ = 0.49, CR = 16, and T_{in} = 476 K

Mix 1: 40 % n-dodecane, 60 % iso-cetane
Mix 2: 37 % n-dodecane, 63 % methylcyclohexane
Mix 3: 51 % n-dodecane, 49 % 1-methylnaphthalene

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In our PFR experiments, a mixture of 43% n-dodecane, 27% iso-cetane, 15% methylcyclohexane, and 15% 1-methylnaphthalene was shown to match the low and intermediate temperature reactivity of the average JP-8 sample, #3684. For further exploration of this mixture as a JP-8 surrogate, it was run in the engine test facility at equivalence ratios of 0.20, 0.32, and 0.35. Figs. 5 and 6 show the pressure traces for the $\phi = 0.20$ and 0.32 experiments, respectively; the $\phi = 0.35$ data have slightly shorter ignition times than the $\phi = 0.32$ data. The results with this mixture matched the average behavior of JP-8 and Jet A to within ~1.5 CAD, suggesting that a surrogate fuel developed in a pressurized flow reactor mimics the corresponding autoignition behavior in an engine.
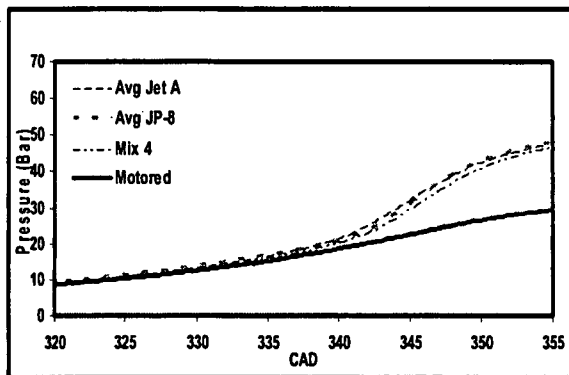

Figure 5: Comparison of the average JP-8 and Jet A samples and the surrogate mixture (Mix 4) at $\phi = 0.20$, CR = 16, and $T_{in} = 476$ K
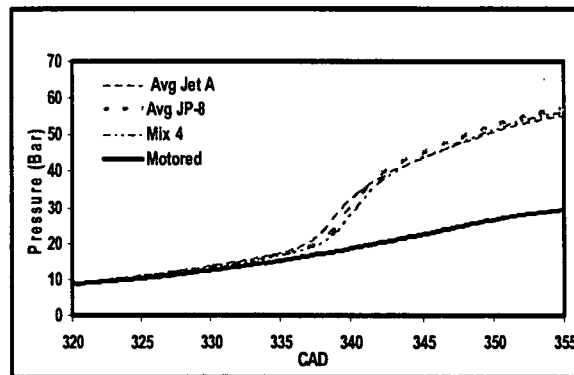
Figure 6: Comparison of the average JP-8 and Jet A samples and the surrogate mixture (Mix 4) at $\phi = 0.32$, CR = 16, and $T_{in} = 476$ K

In our PFR facility, the oxidation of Fischer-Tropsch JP-8 (100% alkanes) and its potential surrogate was explored. The PFR was designed to study the effects of temperature and pressure on the oxidation of hydrocarbon species at temperatures of 600 – 1000 K and pressures of 2 – 20 atm with relative isolation from fluid mechanics and temperature gradients. Synthetic air is formed by mixing nitrogen and oxygen. The liquid fuel is injected into a separate stream of nitrogen for vaporization. This vaporized fuel and the synthetic air are injected into the reactor in an opposed jet nozzle. The mixture then flows into a quartz reaction tube. A gas sampling probe is moved inside the reactor tube to collect oxidized samples from the reaction zone at selected reaction times or positions. For these experiments, the PFR was preheated to 800 K and once the reaction stabilized, the PFR was cooled at a rate of 2-5 K/min. During this cool down, CO and CO_2 were continuously monitored. All of the experiments were run at 8 atm pressure, 0.30 equivalence ratio, 120 ms residence time, and 80.0% N_2 dilution in the fuel.

Figs. 7 and 8 show the CO and CO_2, respectively, produced by the petroleum-derived JP-8 (#3684) and Fischer-Tropsch JP-8 (#4734) samples. In the low and intermediate temperature regimes of hydrocarbon oxidation, the negative temperature coefficient (NTC) region is considered to start when the reactivity of the fuel, as represented by CO production, decreases with increasing temperature. Competition between different reaction paths causes this phenomenon. In these experiments, the NTC region for petroleum-derived JP-8 started at 692 K, where it produced 600 ppm CO. The NTC region for Fischer-Tropsch JP-8 started at approximately the same temperature, 690 K, yet it produced much more CO, 890 ppm.
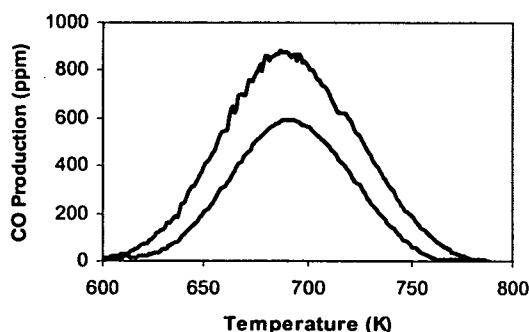
Fig. 7: CO production of Fischer-Tropsch (upper) and petroleum-derived (lower) JP-8's in the PFR
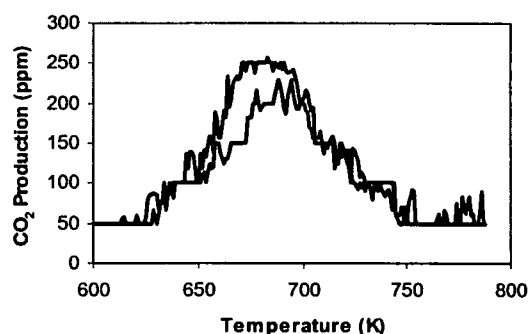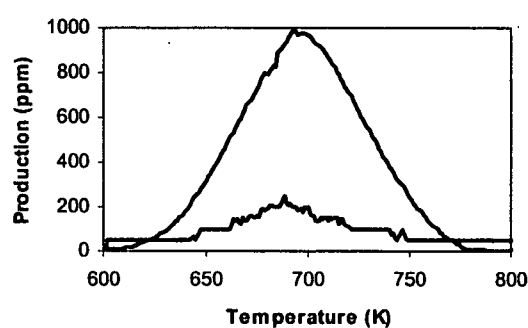
Fig. 8: CO₂ production of Fischer-Tropsch (upper) and petroleum-derived (lower) JP-8's in the PFR

While petroleum-derived JP-8 consists of approximately 60% alkanes, 20% cycloalkanes, and 20% aromatics, Fischer-Tropsch JP-8 consists of 100% alkanes. The petroleum-derived JP-8 formed significantly less CO because the 40% cycloalkanes and aromatics produce a much lower CI and also because the aromatics act as radical scavengers. This implies that different surrogates may be necessary for petroleum-derived and Fischer-Tropsch JP-8's. Thus, while Mix 4, as defined above, may be appropriate for petroleum-derived JP-8, the development of a surrogate for Fischer-Tropsch JP-8 is necessary.

As a first step, the autoignition reactivity of linear and branched alkanes, n-decane and iso-octane, respectively, were investigated as surrogate components. Figs. 9 and 10 show the CO and CO_2 production of neat n-decane and a mixture of 59.4% n-decane/40.6% iso-octane, respectively. n-Decane produced a maximum CO concentration of 1790 ppm at 707 K, while the mixture produced a maximum CO concentration of 990 ppm at 694 K. The mixture produced 100 ppm more CO than the Fischer-Tropsch JP-8, and thus a slight adjustment of the mixture composition should properly match the low temperature reactivity.
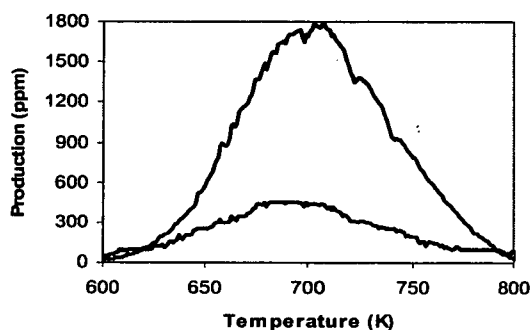
Fig. 9: CO (upper) and CO₂ (lower) production of n-decane in the PFR

Fig. 10: CO (upper) and CO₂ (lower) production of 59.4% n-decane/40.6% iso-octane mixture in the PFR

In summary, recent studies have focused on examining jet fuels and a JP-8 surrogate in an engine and on exploring a Fischer-Tropsch JP-8 surrogate in a flow reactor. Future work will focus on identifying and quantifying intermediate species in both sets of experiments, as was previously done with the JP-8 surrogate in the flow reactor.